Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Tough Strained Fibers of Polyelectrolyte Complex: Pretensioned Polymers

*Qifeng Wang, and Joseph B. Schlenoff**

Strain Release

Samples of extruded PEC, exPEC, were relaxed in solutions of salt at room temperature or salt-free hot water. Fig. S1 shows the final length attained by samples. All lengths are normalized to the starting length (3 to 4 cm).

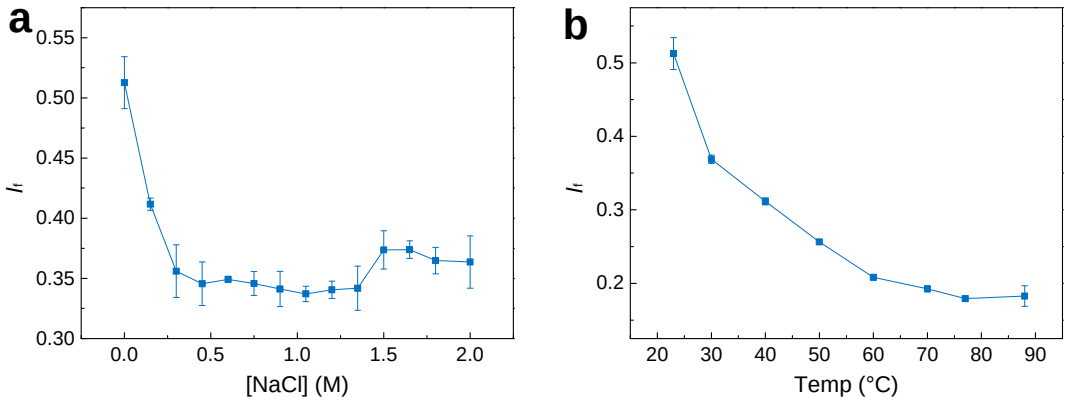

Fig. S1 Final length (l_f) of exPEC samples in (a) NaCl: (b) and hot water. These points are the averages of the last 3 measurements in relaxation curves shown in Fig. 2a and 2b.

Fitting Constants for Strain Release

When the temperature is lower than the T_g of the exPEC ([NaCl] ≤ 0.75 M and T ≤ 30 °C), an additional process of rate constant (k_2) is needed for reasonable fits. The equation has two exponential decays:

$$l_t = l_f + A_1 e^{-k_1(t-t_h)} + A_2 e^{-k_2(t-t_h)} \quad \text{(S1)}$$

where k_1 and k_2 are the rate constants. A_1 and A_2 are contributions from the two relaxation processes (i.e. the weights of the two exponential decays). $l_f + A_1 + A_2 = 1$.

The linear fits for k_1 are:

$\ln k = -8.38 + 0.90\ [\mathrm{NaCl}]^{6/5}$ ($r^2 = 0.971$) for the salt samples

$\ln k = 15.7 - 6940\ (1/T)$ ($r^2 = 0.981$) for the hot water samples.

These fits were used to plot the equivalence of [NaCl] and temperature in Fig. 5b.

The parameters for fitting are given in Tables S1 and S2 below.

Table S1. Fitting parameters for relaxation in NaCl solutions.

NaCl [M]	Temp [°C]	I_f	t_h	$(1-I_f)$ or A_1 [a)]	k_1 $\times 10^{-4}$	A_2 [b)]	k_2 $\times 10^{-6}$	r^2
0	23	0.528	713	0.165	3.00	0.306	5.64	0.992
0.15	23	0.428	965	0.239	2.26	0.333	6.13	0.993
0.3	23	0.368	907	0.358	2.79	0.274	10.9	0.994
0.45	23	0.355	764	0.440	3.07	0.205	19.8	0.995
0.6	23	0.355	1234	0.455	3.75	0.190	41.0	0.997
0.75	23	0.350	1217	0.507	4.66	0.143	61.5	0.997
0.9	23	0.350	1576	0.650	4.71			0.989
1.05	23	0.342	1063	0.658	4.88			0.989
1.2	23	0.346	1344	0.654	6.89			0.988
1.35	23	0.346	1180	0.654	8.94			0.997
1.5	23	0.365	1220	0.635	9.61			0.994
1.65	23	0.371	1070	0.629	12.1			0.994
1.8	23	0.363	1001	0.637	14.1			0.995
2	23	0.364	958	0.636	20.5			0.999

[a)] $1 - I_f = A_1 + A_2$ for two processes of rate constant and $1 - I_f = A_1$ for one process of rate constant.

Table S2. Fitting parameters for relaxation in water.

NaCl [M]	Temp [°C]	I_f	t_h	$(1-I_f)$ or A_1 [a)]	k_1 $\times 10^{-4}$	A_2 [b)]	k_2 $\times 10^{-6}$	r^2
0	23	0.528	713	0.165	3.00	0.306	5.64	0.992
0	30	0.371	384	0.418	8.09	0.211	51.7	0.990
0	40	0.348	254	0.652	18.0			0.981
0	50	0.284	131	0.716	37.6			0.985
0	60	0.223	74	0.777	65.7			0.991
0	70	0.207	46	0.793	106			0.986
0	77	0.201	32	0.799	151			0.991
0	88	0.188	14	0.812	239			0.996

[a)] $1 - I_f = A_1 + A_2$ for two processes of rate constant and $1 - I_f = A_1$ for one process of rate constant.

Swelling

The hydration time was interpreted to be the time taken before the samples started relaxing (seen in Fig. 2 as a short induction period before relaxation starts). Hydration times for individual samples were obtained from the fits, and are shown in Fig. S2

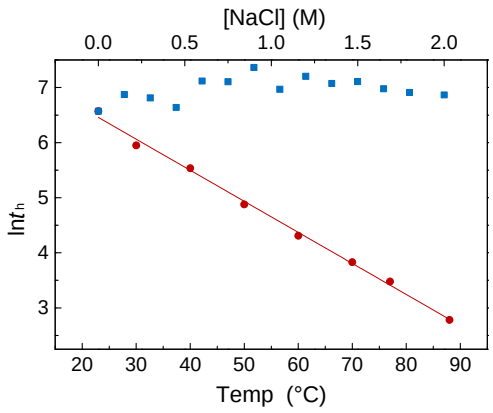

Fig. S2 Hydration time (t_h) for different [NaCl] (■); and different temperatures of water (●). t_h does not change much with [NaCl] but decreases with increasing temperature. Hydration times used in fitting are also given in Tables S1 and S2.

Mechanical Test of Removed Rivets

The exPEC "rivets" were excised, by cutting one of the caps off, from the sample shown (holding the two aluminum bars together) in Figure 6. The toughness of fastened exPEC rivets was measured by strain-to-break experiments (Figure S3). The rivets break at a strain of about 20% with a mean toughness of 5.5 ± 0.8 MJ m^{-3}.

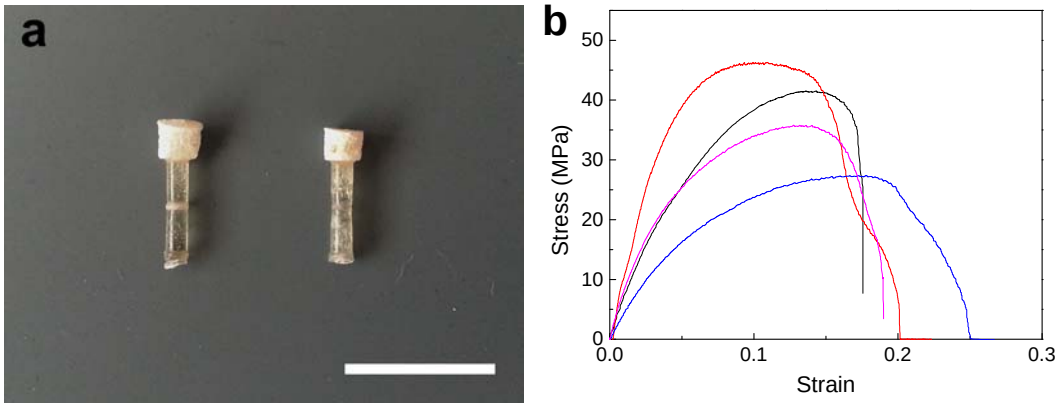

Fig. S3. Photograph of two exPEC rivets removed from the fastened aluminum bars in Fig. 6 of the main paper (a) and strain-to-break test for all four excised rivets (b). Scale bar in **a** is 1 cm.

References

[1] J. B. Schlenoff, A. H. Rmaile, C. B. Bucur, *J. Am. Chem. Soc.* **2008**, *130*, 13589.
[2] R. F. Shamoun, A. Reisch, J. B. Schlenoff, *Adv. Funct. Mater.* **2012**, *22*, 1923.